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Electrical transport and magnetic studies of $Nd_{1-x}Ca_xSr_2Cu_2FeO_\delta$ compounds

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Abstract

We have measured the temperature dependence of the DC electrical resistivity and susceptibility in the interval 4.2–300 K for $Nd_{1-x}Ca_xSr_2Cu_2FeO_\delta$ ($x = 0.0, 0.1, 0.2$ and 0.3). Analysis of the results showed the density of states to be a strong function of x, indicating the existence of short range fluctuations near the Fermi level E_F. The magnetic susceptibility, however, shows the oxidation state of Fe remains at $+3$ for $x \geq 0$.

To elucidate the mechanism of superconductivity, we have measured the electrical transport and magnetisation of $Nd_{1-x}Ca_xSr_2Cu_2FeO_\delta$ compounds for $x = 0.0$, 0.1, 0.2 and 0.3. XRD data revealed that the system remained single phase in this composition range, i.e. $0 \leq x \leq 0.3$, and crystallised into a tetragonal symmetry. The values of the lattice constants were found to be unchanged with varying Ca concentration. This is consistent with the TGA experiments, which showed that the oxygen content remained constant at $\sim 7.12(\pm 0.02)$ for all values of x. The fixed values of the oxygen content agrees with neutron diffraction results carried out on a similar kind of system [1]. In Fig. 1, for $x \geq 0$, the resistivity is shown to increase with decreasing temperature, indicating a semiconducting-type behaviour. Such behaviour could be ascribed to a phonon assisted type of hopping process arising due to localisation of charge carriers near E_F. In this case the resistivity could be expressed in general form as

$$\rho(T) = \rho(0)\exp(T_0/T)^p, \qquad (1)$$

where $p = 1$ corresponds to nearest neighbour hopping [2], $p = 1/2$ corresponds to a hopping process with Coulomb interaction, between localised charge carriers, taken into account [3] whereas $p = 1/3$ and $1/4$ correspond to variable range hopping for two- and three-dimensional systems [4], respectively. In order to find the correct form of resistivity the data were plotted as $\ln \rho(T)$ versus $1/T$ for various values of p. Surprisingly, for $x = 0.0$ and 0.2 the data showed the preference of $p = 0.25$ (see Fig. 2), whereas $p = 0.5$ for $x = 0.1$ and 0.3 (see Fig. 3). To confirm values of p further, $d\ln(\rho)/dT^{-1}$ was plotted against temperature on the log–log scale. The experimental values of p were found close to ~ 0.5 and 0.25 for the respective systems. Similar behaviour was observed by Ellman et al. [5] in the $La_{2-x}Sr_xCuO_4$ system by varying x. Here $p = 0.5$ corresponds to a dip in the density of states (DOS), leading to the formation of a soft Coulomb gap near E_F, due to correlation effects. This effect becomes more prominent when the overlap of the impurity wave functions diminishes and the localisation length reduces to a much smaller value than the distance between impurity centres.

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The continuous variation of p, in a *periodic* manner, indicates an appearance and disappearance of the gap as x is increased. This could be attributed to the short range fluctuations in the DOS with respect to energy near E_F. The values of T_0, estimated from the respective slopes, were found as 6.25×10^6 K, 8×10^6 K and 2458 K, 1283 K. The localisation length α can be calculated using

$$\alpha_M = \{2\Pi(k_B T_0)N(E_F)/3 \times 2^4\}^{-1/3} \text{ Å}, \quad (2)$$

$$\alpha_{ES} = e^2/k_B T_0 \kappa \text{ Å}, \quad (3)$$

for the Mott [4] and Efros–Shklovskii [3] models, respectively. Here $N(E_F)$ is the constant DOS at the Fermi level and κ is the dielectric constant. For $x = 0.0$ and 0.2, choosing $N(E_F) \sim 1$ state/eV cell, values of α_M were estimated in the range ~ 0.2–0.3 Å. Similarly α_{ES} values were also obtained for the $x = 0.1$ and 0.3 systems in the range 0.5–1.03 Å for $\kappa = 100$ [5]. These values of α are much smaller than the interatomic distance, thereby indicating a strong localisation of charge carriers in the system. This could be due to the system falling in the close regime or boundary of the insulator–metal transition, causing fluctuations in the DOS in the vicinity of E_F. According to Efros and Shklovskii [6], such fluctuations within or in the proximity of the gap could lead to different values of p. This explains, therefore, why p is a function of x. In Fig. 4, the temperature dependence of the magnetic susceptibility is depicted for $x \geq 0$ in the temperature range 4.2–250 K. The data were fitted to $\chi(T) = \chi_0 + 3k_B\mu_{eff}^2/(T + \Theta)$.

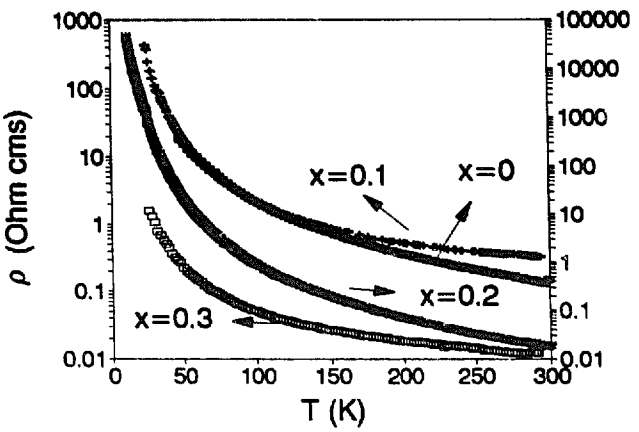

Fig. 1. Temperature dependence of the resistivity of $Nd_{1-x}Ca_xSr_2Cu_2FeO_\delta$ for $x = 0.0$, 0.1, 0.2 and 0.3.

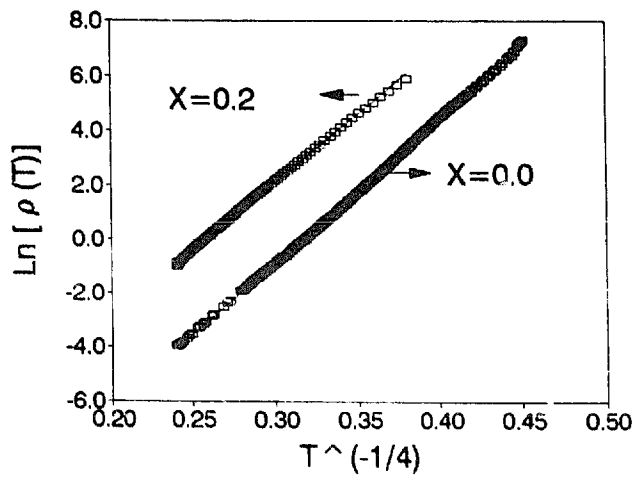

Fig. 2. Plot of $\ln \rho(T)$ against $T^{-1/4}$ for $x = 0.0$ and 0.2, exhibiting variable range hopping conduction as given by Mott [2]. Here the solid line indicates a calculated value.

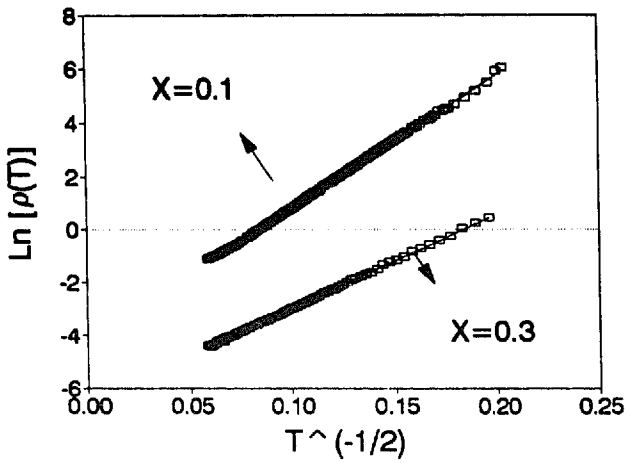

Fig. 3. Plot of $\ln \rho(T)$ against $T^{-1/2}$, for $x = 0.1$ and 0.3, indicating the existence of a soft Coulomb gap. Here the solid line indicates a theoretical value.

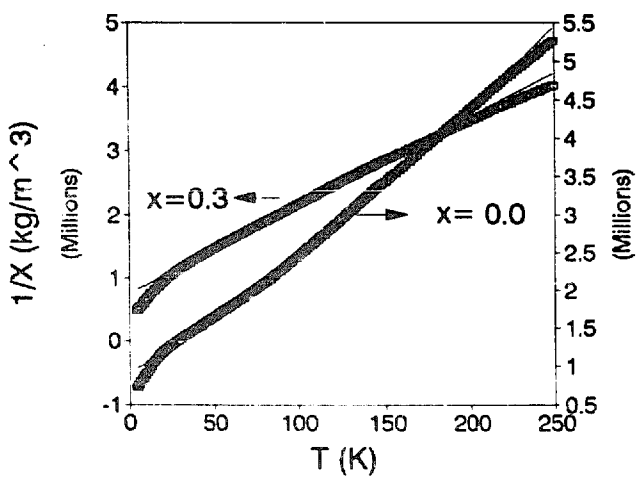

Fig 4. Demonstration of Curie Weiss behaviour for $x = 0.0$ and 0.3. The solid line corresponds to a calculated value.

All the curves exhibited a Curie–Weiss behaviour with deviations below 20 K as shown in Fig. 4 (for clarity only the data for $x = 0.3$ and $x = 0$ are shown). The value of μ_{eff} was found constant as $5.36\mu_B$ for all values of x. This value is less than the combined values of the magnetic moments calculated for Nd^{+3} and Fe^{+3} free ions. This could be attributed to the compensation of spins due to antiferromagnetic exchange interaction taking place between Nd^{+3} and Fe^{+3} ions as shown by the significant values of Θ observed in the range 55–75 K. Alternatively, Fe^{+3} spins could be considered as dominating in the system due to the fact that the experimental value of μ_{eff} falls reasonably close to the free ion value of Fe^{+3}, i.e. $5.92\mu_B$. If this is true then the result indicates that Fe remains in the $+3$ oxidation state for $x \geq 0$. On the other hand, χ_0 was found positive with values in the range $(5.14\text{–}8.65) \times 10^{-8}\ m^3/kg$ and negative in the range $(2.6\text{–}6.2) \times 10^{-8}\ m^3/kg$ for $x = 0$, 0.2 and 0.1 and 0.3, respectively. A systematic variation of χ_0, with increasing x, from positive to negative can be taken as a clue towards a change in DOS near E_F. This is in accordance with values of p varying in a similar fashion with x.

References

[1] E. Suard, V. Caignaert, A. Maignan and B. Raveau, Physica C 182 (1991) 212.

[2] A. Miller and S. Abrahams, Phys. Rev. 120 (1960) 745.

[3] A.L. Efros and B.I. Shklovskii, J. Phys. C 8 (1975) L49.

[4] N.F. Mott, in: Conduction in Non-Crystalline Materials (Clarendon Press, Oxford, 1987) p. 27.

[5] B. Ellman, H.M. Jaeger, D.P. Katz and T.F. Rosenbaum, Phys. Rev. B 39 (1989) 9012.

[6] B.I. Shklovskii and A.L. Efros, in: Electronic Properties of Doped Semiconductors (Springer, Berlin, 1984) p. 202.